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On the validity of the Kelvin equation

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Abstract. The Kelvin equation for the equilibrium vapour pressure outside a drop of liquid is widely quoted but its derivation is subject to three assumptions which are not obviously justified. Consequently some doubt has recently been thrown on the value of the equation for estimating the true vapour pressure. It is shown in general, and explicitly and in detail for a Lennard-Jones fluid, that the equation is valid to a few per cent even for temperatures approaching the critical temperature and for microscopic drops insofar as homogeneous thermodynamics is valid. It is noted that the spinoidal radius of a drop is numerically equal to the surface thickness for a Lennard-Jones fluid. This relation may well be general and useful.

1. Introduction

For a spherical liquid-vapour surface with radius of curvature R the difference of pressure Δp between the two regions is given by the Laplace equation (see Rowlinson and Widom 1982 p 21, ref 10)

$$\Delta p = 2\gamma/R. \quad (1.1)$$

This is a fundamental equation in the thermodynamics of surfaces and is virtually a definition of the surface tension γ .

If we have a drop of liquid in equilibrium with its vapour it is useful and common to derive another equation, which is usually, but not invariably, called the Kelvin equation (Thomson 1871, see Rowlinson and Widom 1982, p 48, ref 26)

$$p_{\text{KK}}/p_v = \exp[(2\gamma/R)(1/\rho_l kT)]. \quad (1.2)$$

ρ_l is the number density of the liquid well inside the drop, p_v is the vapour pressure, i.e. outside a plane surface ($R \rightarrow \infty$), and p_{KK} is the Kelvin pressure well outside a drop of radius R in the Kelvin approximation, i.e. as defined by (1.2).

Since the Kelvin equation, (1.2), involves several approximations (see § 2) we distinguish this approximate value p_{KK} from the exact thermodynamic value of the pressure outside the drop, which we shall call p_K . This paper is mainly concerned with the difference between p_{KK} and p_K .

The Kelvin equation can be derived in a number of ways and several approximations are introduced in various ways, for example, see Guggenheim (1949), Becker (1967), Rowlinson and Widom (1982) and Adkins (1983). The equation is useful and important. Its most familiar general use is in noting that, since a large drop in equilibrium has a smaller Kelvin pressure p_K than a smaller drop, in a mixture of drops, the larger drops grow at the expense of the smaller ones. Indeed this is a simple explanation of why

a supersaturated vapour condenses, if it can, to a bulk liquid in equilibrium with its vapour and that drops are scavenged from the vapour by the bulk liquid, if one is present. It is of rather general interest, therefore, to consider the validity of such a widely used formula. This was briefly discussed earlier by Melrose (1966) for liquid argon at its boiling point.

The matter is also of interest because the Kelvin formula has recently been tested in connection with the simulation of microscopic liquid drops, $R/\sigma \approx 2-10$, in equilibrium with their own vapour (Powles *et al* 1983a, Thompson *et al* 1984). For very small drops, of course, the validity of the use of thermodynamics for very inhomogeneous systems arises. In particular the possible curvature dependence of surface tension and the precise meaning of the 'radius' of the drop (Tolman 1948) require consideration; for a detailed discussion see Rowlinson and Widom (1982) and Henderson (1985). These matters can only be resolved by generalised thermodynamics or statistical mechanics and remain somewhat controversial. However, as far as the Kelvin equation is concerned, some authors have cast doubt on its validity (Thompson *et al* 1984, Henderson 1985), not only because of the curvature effect on γ and on the precise meaning of R , but also because of the above-mentioned approximations in the thermodynamic derivation. The latter problem, at least, can be dealt with very simply and we do that in this paper. We show that the approximations made are much less important, even at high temperatures, than might be supposed.

2. The Kelvin equation

The most elegant way of obtaining the Kelvin equation is given by Rowlinson and Widom (1982 p 42). They point out that (we retain their notation for the moment) the chemical potential is the same both inside (α) and outside (β) the drops (indeed everywhere) whether it has a finite radius R or an infinite radius (i.e. the plane surface) so that

$$\mu_R^\alpha = \mu_R^\beta \quad \text{and} \quad \mu_\infty^\alpha = \mu_\infty^\beta. \quad (2.1)$$

Hence

$$\mu_R^\alpha - \mu_\infty^\alpha = \mu_R^\beta - \mu_\infty^\beta. \quad (2.2)$$

However, $dp = \rho d\mu + s dT$ and so at constant T we have

$$d\mu = dp/\rho. \quad (2.3)$$

Thus integrating gives

$$\int_{p_\infty^\alpha}^{p_R^\alpha} \frac{dp}{\rho^\alpha} = \int_{p_\infty^\beta}^{p_R^\beta} \frac{dp}{\rho^\beta}. \quad (2.4)$$

Now $p_\infty^\alpha = p_\infty^\beta = p_v$, the usual vapour pressure; p^β is what we call p_K and using (1.1), $p_R^\alpha = 2\gamma/R + p_K$. Writing $\rho^\alpha = \rho_l(p)$ and $\rho^\beta = \rho_v(p)$ gives

$$\int_{p_v}^{2\gamma/R + p_K} dp/\rho_l(p) = \int_{p_v}^{p_K} dp/\rho_v(p). \quad (2.5)$$

If (1) the liquid is incompressible at ρ_l , the coexistence value, and (2) the vapour is a perfect gas we find from (2.5) that

$$kT \ln(p_K/p_v) \approx \frac{1}{\rho_l} \left(\frac{2\gamma}{R} + p_K - p_v \right).$$

If (3) $2\gamma/R \gg p_K - p_v$, then we obtain the Kelvin equation (1.2), giving the estimate p_{KK} of p_K and involving the three assumptions (1), (2) and (3).

At low temperatures, near the triple point, the liquid is not very compressible and the vapour has a low density and so is near perfect. Also assumption (3) is quite good as we shall show shortly. However, as the temperature increases the isothermal compressibility χ increases (it diverges at the critical point). The vapour pressure, and more so the Kelvin pressure, increase rapidly (Arrhenius) so that vapour rapidly becomes very imperfect. These facts are illustrated in table 1 for a 'Lennard-Jones' fluid. It would appear, therefore, that the Kelvin equation would become useless at high, and even possibly moderate, temperatures. However, this is too simplistic a view. Consider the three approximations in turn.

(1) The pressure on the liquid inside the drop is $(2\gamma/R + p_K)$ instead of p_v (as it is for the coexisting liquid of density ρ_l). For linear compressibility we have

$$\Delta\rho/\rho_l \sim \chi(2\gamma/R + p_K - p_v). \tag{2.6}$$

But for large enough drops we have from the Kelvin equation itself

$$(p_{KK} - p_v)/p_v \approx (2\gamma/R)/(\rho_l kT). \tag{2.7}$$

Therefore

$$\Delta\rho/\rho_l \sim \chi(2\gamma/R)(1 + p_v/\rho_l kT) \sim \chi(2\gamma/R)(1 + \rho_v/\rho_l) \sim \chi(2\gamma/R). \tag{2.8}$$

This quantity is given in table 1 and it is clear that the assumption of incompressibility of the liquid is good at any temperature except possibly the critical temperature.

(2) The vapour is manifestly imperfect as shown by the compressibility factor in table 1. However, for the Kelvin equation this is not inconsistent with the assumption that the gas is perfect as we now show. Consider the RHS of (2.5) and assume that

$$p = \rho kT. \tag{2.9}$$

Then

$$\text{RHS} \equiv \int_{p_v}^{p_K} \frac{dp}{\rho} = kT \ln(p_K/p_v).$$

Table 1. Some properties, in reduced units, of the Lennard-Jones fluid (see § 3).

T	ρ_l	ρ_v	p_v	χ	$p_v/\rho_v T$	γ^a	$\chi(2\gamma/R)^c$	ρ_l/ρ_v
0.6	0.890	0.000 30	0.000 17	0.054	0.94	1.56	0.017	2970
0.8	0.799	0.0058	0.0044	0.113	0.96	1.05	0.024	138
1.0	0.703	0.0275	0.0237	0.218	0.86	0.60	0.026	26
1.2	0.593	0.087	0.073	0.638	0.70	0.21	0.026	6.8
1.3	0.507	0.158	0.114	2.56	0.56	0.05	0.026	3.2
1.35 ^b	0.349	0.349	0.142	∞	0.30	0	—	1

^a From equation (3.4).

^b T_c .

^c For $R = 10$.

If p_K/p_K is not too large, i.e. R is large enough, then

$$\text{RHS} \approx kT(p_K - p_v)/p_v.$$

But since the vapour is to be assumed perfect consistently we can again use (2.9) and obtain

$$\text{RHS} \approx (p_K - p_v)/\rho_v. \quad (2.10)$$

On the other hand, if p_K and p_v differ little we can assume in the above integral that ρ is virtually constant (not a perfect gas!) at ρ_v and then

$$\text{RHS} \approx (p_K - p_v)/\rho_v \quad (2.11)$$

which is the same as (2.10). Hence the assumption that the gas is perfect is innocuous at any temperature if used consistently, except for very small drops.

(3) Consider $(2\gamma/R)/(p_K - p_v)$. Again use the approximation (2.7) to give

$$(2\gamma/R)/(p_K - p_v) \approx \rho_l kT/p_v \approx \rho_l/\rho_v \quad (2.12)$$

independent of R , after using assumption (2) again.

The ratio, ρ_l/ρ_v , is given in table 1. Clearly approximation (3) is good except very near the critical point. It appears, therefore, that perhaps the Kelvin equation may be more accurate than expected. However, the above argument might be circular because it uses the Kelvin equation to test the Kelvin equation. In fact the conclusion is quite correct and we now give an exact analysis which leads to a quantitative result and the same conclusion.

3. The exact thermodynamic result for the Kelvin pressure for a typical fluid

We can obtain the exact thermodynamic Kelvin equation if we can calculate the chemical potential for the fluid in any thermodynamic state and use the condition

$$\mu_R^\alpha = \mu_R^\beta \quad \text{for } T_\alpha = T_\beta = T. \quad (3.1)$$

We choose $p_K (> p_v)$, which fixes the size of the drop R and calculate μ_R^β . The pressure in the liquid is $(2\gamma/R + p_K)$ at temperature T . We then require that (3.1) be satisfied which determines γ/R for the given value of p_K .

Given the equation of state $p(\rho, T)$ we can calculate μ using the formula (Powles *et al* 1982)

$$\Delta\mu \equiv (\mu - \mu_v) = p/\rho - (p/\rho)_v + \int_{\rho_v}^{\rho} (p/\rho^2) d\rho \quad (3.2)$$

where the subscript v means the value for the coexisting vapour.

We carry out this programme explicitly for the Lennard-Jones (LJ) fluid, i.e. for the central pair-wise interaction potential $\phi(r)$ where

$$\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (3.3)$$

where ε is an energy parameter and σ is a distance parameter.

The equation of state for this fluid has been established by numerous computer simulations, the results of which have been conveniently conflated by Nicolas *et al* (1979) who give $p(\rho, T)$ for a wide range of T and ρ , including the metastable states, in a formula containing 33 parameters. It has been confirmed that this equation of

state gives a reliable value of $\mu(\rho, T)$ by comparison with values obtained, quite independently, by the Widom (1963) method by Powles *et al* (1982) who show that the use of the Nicolas equation, even for metastable states, is fully justified. The coexistence curve, i.e. ρ_l and ρ_v (and p_l and p_v), for the LJ fluid has been reported by Powles (1984) (see table 1).

In the following we work entirely in reduced units, e.g. T is kT/ϵ , ρ is $\rho\sigma^3$, etc. The computation is straightforward and we give only the results. There is, however, one subtlety which must be noted, namely that there is a limit to the maximum value of p_K (or p_{KK}) which can be chosen. The curve of $p(\rho)$ for given T is sigmoidal as illustrated in figure 1. In the density range where $dp/d\rho < 0$ the fluid is mechanically unstable and so we must have $p_K < p_s$ where p_s is the vapour 'spinodal' pressure. As p_K increases from p_v the radius of the drop decreases from infinity and attains a minimum value $R_s(T)$ which we call the spinodal drop radius. This quantity is discussed in § 5.

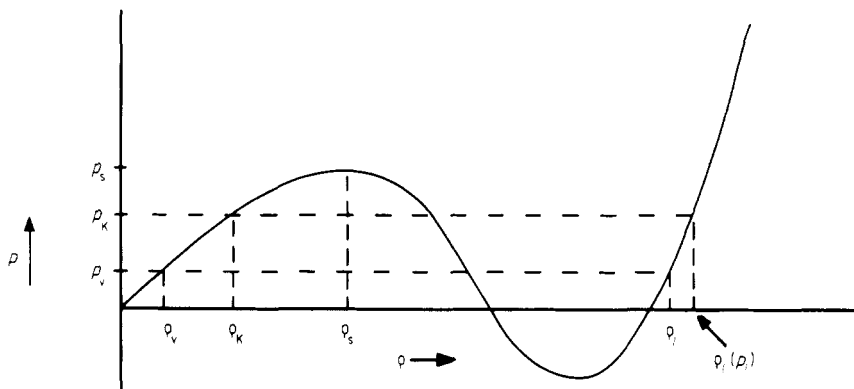


Figure 1. Diagrammatic representation of the pressure of a homogeneous liquid as a function of density at constant temperature. This illustrates the various pressures and densities discussed in the text.

We thus obtain the value of p_K in terms of (γ/R) . But the value of p_{KK} also contains (γ/R) so that p_K and p_{KK} can be compared without a knowledge of γ . This is done in figure 2 for $T = 0.8$. The corresponding radius of the drop is also given (see below). Nevertheless, it is convenient and physically enlightening to evaluate R and to this end we have used the values of γ reported by Chapela *et al* (1977) by simulation of a plane surface. However, these values of γ refer to a LJ fluid with the potential cut-off at $r/\sigma = 2.5$ which significantly changes the equation of state (Powles 1984) and presumably the value of γ . Chapela *et al* (1977) correct for this but there remains some uncertainty in the precise value of γ (Powles *et al* 1983a). However, in the following we shall not incur significant error in using Chapela *et al*'s values of γ adjusted to the correct value of T_c just to obtain R . Their results are conveniently summarised by the 'fit'

$$\gamma \approx 2.24(T_c - T)^{1.26} \tag{3.4}$$

where for the complete LJ potential $T_c = 1.35$. The values of p_K and p_{KK} as a function of $1/R$ at $T = 0.8$ are shown in figure 3. The difference is small but increases with falling radius and p_{KK} is less than p_K .

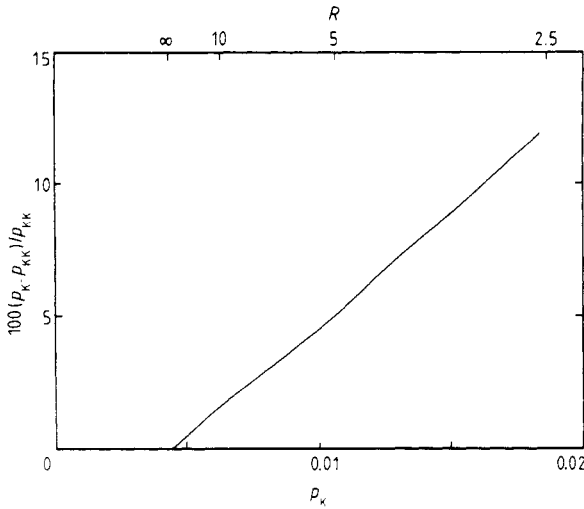


Figure 2. The per cent deviation of the true pressure of the vapour p_K from the Kelvin value p_{KK} as a function of p_K for a Lennard-Jones fluid at reduced temperature 0.8. The upper scale gives the corresponding radius of the drop.

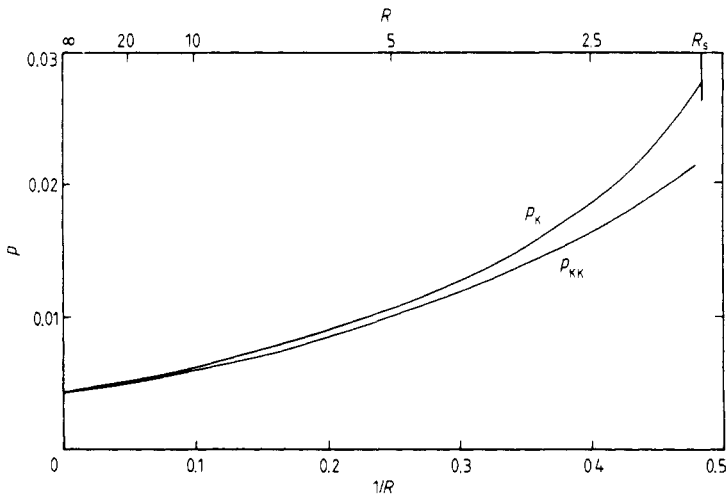


Figure 3. A comparison of the true and Kelvin pressures as a function of reciprocal radius of the drop for a Lennard-Jones fluid at temperature 0.8. The bar corresponds to the spinoidal radius.

The deviation of p_K from p_{KK} is shown in figure 4, as a percentage, as a function of $1/R$ for a series of values of T from slightly below the triple point ($T_c = 0.68$, Hansen and Verlet 1969) almost to the critical point. It should be noted, however, that the results are uncertain near T_c , which is only accessible by extrapolation of simulation results; indeed, Adams (1979) gives $T_c = 1.30$ rather than 1.35.

As expected, the deviation is small at low temperatures even for very small drops. Melrose (1966) came to the same conclusion for liquid argon at $T = 0.73$. It is confirmed that it is also small even at temperatures approaching the critical temperature. For

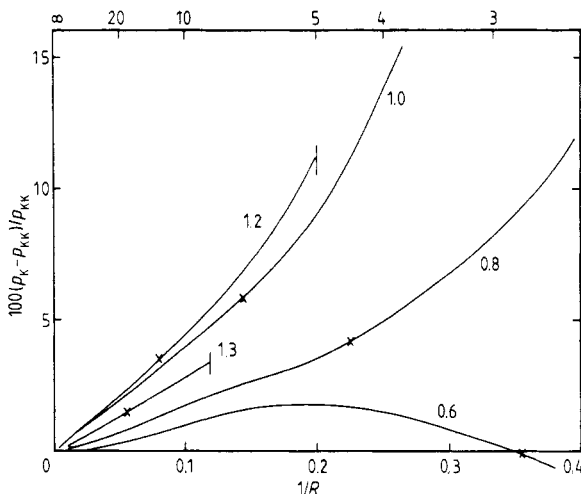


Figure 4. The per cent deviation of the exact thermodynamic pressure outside a drop p_K from that given by the Kelvin equation p_{KK} as a function of reciprocal radius $1/R$ for several temperatures, as indicated, for a Lennard-Jones fluid. The bars for $T = 1.2$ and 1.3 correspond to the spinoidal radius (table 3). The crosses correspond to $R = 2D$.

instance, for $R > 10$ the deviation is less than 5% for any temperature. For argon $\sigma = 3.40 \text{ \AA}$ so that for $R = 10$ the drop has a radius of only 34 \AA and contains only about 3000 atoms. The physical restriction $R < R_s$ is effective in preventing the deviation attaining large values for the higher temperatures. We conclude that the Kelvin equation is much more accurate than might be anticipated.

The true density of the liquid inside the drop is not in fact increased much above the coexistence value as shown in table 2. The vapour becomes very imperfect of course at high temperatures as already illustrated by the compressibility factor $p/\rho T$ in table 1. The exact value of $(2\gamma/R)(p_K - p_v)$ is also given in table 2 and is seen to confirm the approximation ρ_l/ρ_v given in table 1.

At low temperatures, where (3) is a good approximation, the approximations (1) and (2) tend to compensate. Let us assume that the liquid inside the drop is linearly compressible (the isothermal compressibility χ is readily calculated from the Nicolas equation), i.e.

$$\rho_l(p) = \rho_l[1 + \chi(p - p_v)]. \tag{3.5}$$

This gives quite good values of $\rho_l(p_l)$ as shown in table 2. Assume also that the imperfection of the vapour is given by the second virial coefficient only (for values of

Table 2. Some parameters for the LJ fluid and for drops of radius 10 units.

T	$\rho_l(p_l)/\rho_l(p_v)$	$1 + \chi(2\gamma/R + p_K - p_v)$	$(2\gamma/R)/(p_K - p_v)$	$-B_2$
0.6	1.017	1.017	2080	12.7
0.8	1.022	1.024	108	7.82
1.0	1.026	1.027	22	5.32
1.2	1.029	1.031	5.3	3.85
1.3	1.034	1.039	2.0	3.32

B_2 see Barker *et al* 1966), i.e.

$$p/\rho T \approx 1 + B_2\rho. \quad (3.6)$$

Then it can be shown that this approximation to p_K , which we call p_{KA} , is given (with several innocuous further approximations) by

$$\frac{p_{KA} - p_{KK}}{p_{KK}} = \frac{1}{\rho_l T} \frac{2\gamma}{R} \left[\frac{p_v}{\rho_l T} (1 - B_2\rho_l) - \frac{1}{2}\chi \left(\frac{2\gamma}{R} \right) \right]. \quad (3.7)$$

Since $\chi > 0$ and $B_2 < 0$ (for our range of T) the approximations (1) and (2) tend to cancel. The effect of approximation (3) is more subtle and cannot be displayed explicitly. The per cent deviation of p_{KA} from p_{KK} is illustrated in table 3 for $R = 10$. The values are of the same order of magnitude as for the exact values of p_K shown in figure 4. They even show the observed fall in deviation from $T = 1.2$ to $T = 1.3$ but this is no doubt accidental.

Table 3. Comparison of the two approximations to the Kelvin pressure for the Lennard-Jones fluid for $R = 10$. Values of the spinoidal radius R_s and the surface thickness D are also given.

T	$\frac{100(p_{KA} - p_{KK})}{p_{KK}}$	$\frac{100(p_K - p_{KK})}{p_K}$	R_s	D
0.6	-0.3	1.0	1.45	1.41
0.8	1.3	1.8	2.06	2.20
1.0	2.5	3.9	2.89	3.4
1.2	1.9	4.4	4.94	(6.0)
1.3	0.7	2.8	8.33	(8.6)

We must of course bear in mind that the thermodynamic treatment breaks down for very small drops if only because there is then no fluid region inside the drop which can be regarded as a macroscopic liquid and the evaluation of μ has to be modified, e.g. by density-gradient corrections (Evans 1979). Moreover, for small drops the surface tension depends on the curvature (Tolman 1948) and the radius of the drop is ill defined if only because it is comparable with the surface thickness D (see § 4). These matters have also been investigated by the simulation of drops (Powles *et al* 1983b, Thompson *et al* 1984). It is found, as expected, that these effects are appreciable for a drop of radius a few times the surface thickness so that the deviation given in figure 1 will depart from the thermodynamic value for R approaching, say $2D$. D increases with T from about σ to several times σ (D is expected to diverge with the correlation length as T_c is approached) (see table 3). It is to be expected then that the thermodynamic values of p_K are only to be relied on for $R > 2D$, say, and this limit is shown in figure 4. This limit is more severe than $R > R_s$.

4. The Kelvin method for γ

Powles *et al* (1983a) have suggested that it is possible to measure the surface tension γ by using the Kelvin equation and simulation values of the vapour pressure outside

drops of varying radius. If the Kelvin equation is valid a plot of $\ln(p_K/p_v)$ against $1/R$ should be linear with slope $2\gamma/\rho_l T$ from which γ can be measured.

In figure 5 we compare the exact value of $\ln(p_K/p_v)$ with the Kelvin value for several temperatures for the LJ fluid. We see that at all temperatures the exact slope is larger than that for the Kelvin equation and the discrepancy increases with increasing temperature. Exactly this effect was found by Powles *et al* (1983a) for a simulation of LJ drops at $T = 0.84$ except that there was a fall in $\ln(p_K/p_v)$ for the smallest drop, with $R = 3.5$, which they attributed to a curvature dependence of γ with a Tolman length ~ 0.5 but which of course might also be due to the invalidity of ‘homogeneous’ thermodynamics.

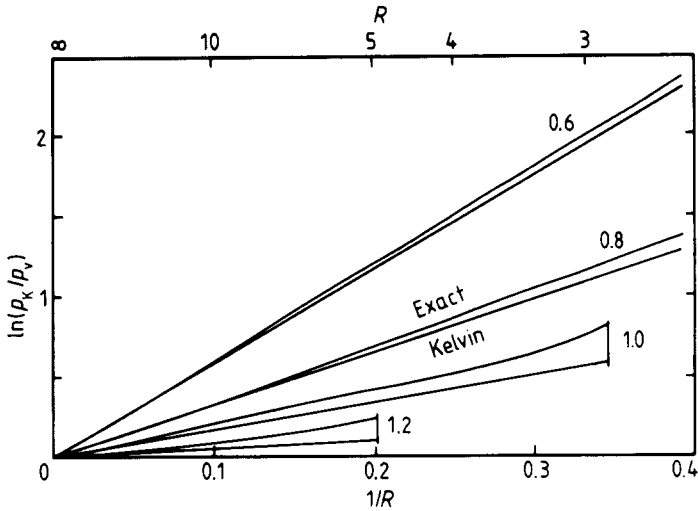


Figure 5. Plots of $\ln(p_K/p_v)$ against $1/R$ for the LJ fluid at various temperatures as indicated (upper curve of each pair). Also given are the Kelvin lines, i.e. $\ln(p_{KK}/p_v) = (2\gamma/\rho_l T)(1/R)$ (lower straight lines of each pair).

Thomson *et al* (1984) have also measured the vapour pressure outside a drop by a different method. They observe that $\ln(p_K/p_v)$ falls *below* the Kelvin line. They suggest that one reason the Kelvin equation cannot be used is because of the three assumptions discussed in this paper. We can certainly remove this as a source of the difficulty since, as shown in figure 5, lifting these assumptions has little effect under their conditions and what little effect there is raises $\ln(p_K/p_v)$ *above* the Kelvin line.

5. An empirical relation between the spinoidal radius and the surface thickness

The surface thickness of LJ drops is reported by Powles *et al* (1983b) for three temperatures. Interpolated and extrapolated values of the thickness parameter, D , are given in table 3. The values at the two higher temperatures are rather uncertain. These may be compared with the values of the spinoidal radius R_s , which requires a knowledge of the surface tension γ .

We conclude that

$$R_s \approx D. \tag{5.1}$$

If this relation is generally true it is remarkable and useful. It is remarkable because R_s is obtained from simple macroscopic measurements, the equation of state and the surface tension, whereas D is a microscopic quantity which is very difficult to measure. It is useful because it may be used to predict values of D from $p(\rho)$ and γ . As far as we are aware there are no other fluids than LJ for which sufficient data exist for a test of the generality of the postulate (5.1) to be made.

Acknowledgment

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